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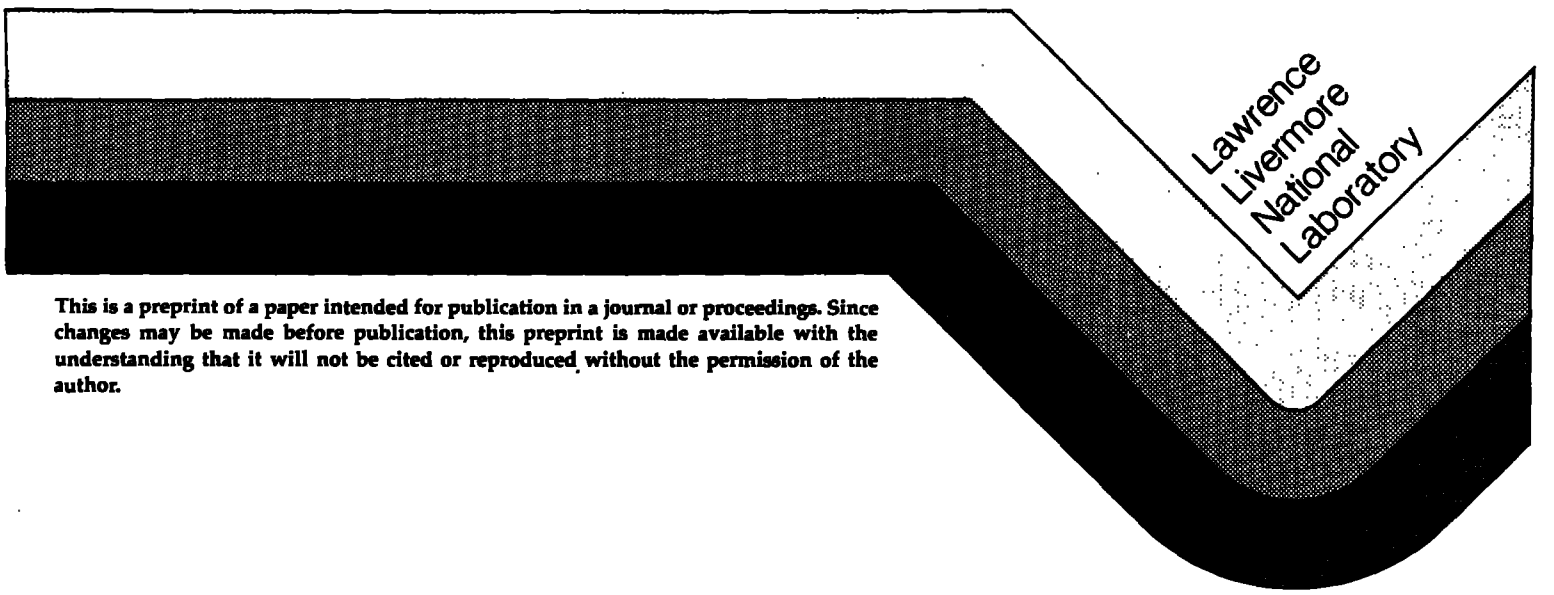

THE DISSOCIATION OF DENSE LIQUID NITROGEN

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ABSTRACT

A theoretical model has been developed to examine the dissociation of shock compressed liquid nitrogen. Calculated shock pressures and shock temperatures are in agreement with experiment. The model correctly predicts the highly unusual feature of a reflected shock point lying above the principal Hugoniot and of a decrease in the temperature of a reflected shock. The shock cooling is shown to be the consequence of a volume dependent dissociation energy.

Introduction

The dissociation of molecular nitrogen has been the subject of several recent experimental and theoretical studies. McMahan and LeSar[1] predicted that the molecular solid at 0 K should dissociate to a monatomic phase near 0.8 Mbar. However subsequent diamond-anvil cell studies have shown no evidence for such a transition up to 1.8 Mbar.[2] The failure to observe this transition has been attributed to a large energy barrier between the two phases.[3] In a series of papers Nellis et al.[4] employing the LLNL two stage light gas gun have reported shock wave measurements which show that liquid nitrogen begins to undergo a transformation at a pressure of 0.31 Mbar and a temperature of about 7000 K. The most likely explanation is that they have observed molecular dissociation. More recently Radousky et al.[5] have reported shock temperature measurements for this material along the principal and reflected Hugoniots and also of the electrical conductivity along the principal Hugoniot.

One of the earliest shock wave studies on molecular nitrogen was carried out by Christian et al.[6] They used an explosive shock tube to compress the gas initially at room temperature and 580 mm pressure. The object of that study was to determine which of two conflicting values of the dissociation energies, 9.76 or 7.38 ev., was correct. In the case of a gas the equation of state is quite simple, and the Hugoniot can be predicted exactly. Only the energy absorbed in the dissociation process can alter the Hugoniot. The two energies are sufficiently different so as to provide a clear cut choice. Christian et al. determined that only the former value will predict a Hugoniot curve that agrees with experiment and this remains the currently accepted value. For the case of a dense liquid the uncertainties in the composition,

intermolecular forces and statistical mechanics of the mixture present a considerably more difficult problem.

The objective of this paper is to derive a theoretical model to examine the experimental data and provide insight into the atomic and molecular physics of the dense dissociating fluid. In the next section we examine a sequence of models of increasing complexity for the purpose of isolating the essential features of a 'successful' theory. Our presentation is frankly pedagogic and we proceed along the path we actually traveled in building the model. This, we believe, provides a clearer presentation of the theoretical problems and approximations.

Theoretical Models

As a point of reference we begin our study with a model that neglects dissociation and only considers a fluid of interacting molecules. We then advance to a "textbook" treatment of the dissociation of molecules into free atoms employing the law of mass action with a constant value of the dissociation energy. The model fails because it does not properly consider the cohesive energy of the atomic phase. This feature is introduced in the final part of this section and the resulting model is shown to agree with most of the experimental data.

A) The Liquid N_2 Hugoniot.

The Hugoniot of liquid nitrogen has been calculated by a number of authors.[7,8,9] In the simplest model, the one which neglects dissociation, the intermolecular potential is described by a spherical angle averaged interaction. This has been shown to be a good approximation along the

Hugoniot. The vibrational and electronic energy levels are taken to be the free molecule values.[7]

The exponential-six (exp-6) potential has been used extensively in the study of many dense liquids including nitrogen.

$$\phi(r) = \epsilon\left[\left(\frac{6}{\alpha - 6}\right) \exp[\alpha(1 - r/r^*)] - \left(\frac{\alpha}{\alpha - 6}\right)\left(\frac{r^*}{r}\right)^6\right] \tag{1}$$

In the present study $\alpha = 13.2$, $r^* = 4.09$ A and $\epsilon/k = 101.9$ K. Except for the first these values are nearly the same as those used in a previous study. The parameters were chosen to scale from the argon potential by the use of the law of corresponding states'. Earlier work[7] had suggested a value for of 13.0. But the difference in the predicted Hugoniots are quite minor and either value will provide a satisfactory fit to the undissociated portion of the Hugoniot.

In the present paper we use the same fluid theory as we have in our earlier work[7] where the Helmholtz free energy is written as the sum of the free energies of all degrees of freedom

$$\beta A = \beta A_t + \beta A_r + \beta A_v + \beta A_e + \beta A_{int} \ . \tag{2}$$

The explicit expressions for the first four terms are well known. They are respectively, the translational, rotational, vibrational and electronic free energies. The last term A_{int}, the interaction free energy, has been computed by soft sphere variational theory[10] using the free energy of the inverse twelfth power potential as the reference

$$A_{int} \leq A_{HS}(\eta) + F(\eta)\ NkT + \frac{N^2}{2V} \int_d^\infty \phi(r)\ g_{HS}(r, \eta)\ d\bar{r} \quad , \tag{3}$$

where V is the volume and

$$A_{HS} = \frac{4\eta - 3\eta^2}{1 - \eta^2} NkT, \quad F(\eta) = -(\eta^4/2 + \eta^2 + \eta/2) \quad .$$

$g_{HS}(r, \eta)$ is the hard-sphere radial distribution function based on the Percus-Yevick equation. All of these terms are functions of the hard-sphere packing fraction $\eta = (\pi/6)N/Vd^3$, where d is a hard-sphere diameter. The appropriate η (or d) is the one that minimizes the rhs of Eq. (3), because the internal degrees of freedom are independent of density (hence, η).

The pressure (P) and total energy (E) may be computed using thermodynamic relations

$$\frac{\beta PV}{N} = 1 - \left(\frac{V\beta\partial A_{int}}{N\partial V}\right)_T = 1 + \frac{P_{int}V}{NkT} \tag{4}$$

and

$$\frac{\beta E}{N} = \frac{3}{2} + \left(\frac{\partial \beta A_{int/N}}{\partial \beta}\right)_V + \beta E_{rve} \quad . \tag{5}$$

The energy E_{rve} of the internal degrees of freedom is given by

$$\beta E_{rve} = \frac{n}{2} + \left(\frac{\beta h\nu}{2} + \frac{\beta h\nu}{e^{\beta h\nu} - 1}\right) - \frac{\partial}{\partial \beta} \ln q_e \tag{6}$$

The first term corresponds to a contribution by n degrees of rotational freedom (two for diatomics, three for nonlinear polyatomics). The second term is the vibrational energy. For N_2 $h\nu/k = 3392$ K. The electronic partition function for N_2 is

$$q_e^{N_2} = 1 + 3e^{-6.167/T} + 3e^{-7.351} + e^{-8.546/T} \tag{7}$$

where T is the temperature in electron volts (eV).

The perturbation theory is easily generalized to multicomponent systems.

Hugoniot curves are calculated by finding a (P, V, E) point that satisfies the Hugoniot relation

$$E - E_o = \frac{1}{2} (P + P_o) (V_o - V) \quad , \tag{8}$$

where the subscript zero refers to the initial conditions.

The principal Hugoniot calculated with this model is shown in Fig. 1 (curve A) is in good agreement with the data of Zubarev and Telegin[11] and Nellis et al.[4] up to about 310 kbar. Above this pressure the theoretical curve continues to rise rapidly but fails to exhibit the large increase in compressibilty observed experimentally. Shock temperature measurements provide a very sensitive test of the theory. They have been measured for liquid nitrogen by Radousky et al.[5] and the calculations shown in Fig. 2 exhibit the same pattern of disagreement as the Hugoniot. Clearly this model is incomplete because it fails to incorporate dissociation. The introduction of dissociation with a simple mixture model and a constant value of the dissociation energy (D_o = 9.76 eV) leads to curve B which predicts a small degree of dissociation and a Hugoniot that differs only slightly from curve A.

B) Mixture Model of Molecular Dissociation.

There are a number of reasons why the model might fail even when the dissociation energy is included. For example it does not consider volume dependent shifts in the molecular electronic and vibrational energy levels. These are likely to be important at high temperature and could favor the appearance of the atomic phase. But the most likely cause stems from the neglect of chemical of binding for the monatomic phase. Briefly, we will show that at the conditions of interest the monatomic phase must be a degenerate

metal and a proper model must include the cohesive energy. This leads to a volume dependence in the dissociation energy.

To see why this must be so consider that in the gas phase 9.76 ev are required to break the chemical bond and move the atoms to infinite separation. Clearly this value cannot be correct in the very dense fluid because it does not account for the recombination of atoms into other chemical bonding states. The other group V elements, for example exibit on strong covalently bonded 3-fold coordinated networks which are slight distortions of simple cubic. This binding would return some of the energy expended in the bond breaking and decrease the energy needed for dissociation. An analogous effect known as 'ionization lowering' is observed in dense plasmas where the interaction of the ionized electron with the remaining particles leads to a lowering of the effective ionization energy. We may refer to the molecular analog as 'dissociation lowering.' As an example consider the case in which the molecule in the solid is compressed to such a high density that the molecular bond distance becomes comparable to the intermolecular separation. At this density much less than 9.76 ev would be required to dissociate the molecule. Thus we may conclude that the dissociation energy should decrease continuously from the gas phase value to some much smaller figure at high density.

We have introduced this reasoning into our thermodynamic model by including in the free energy expression below the term E_b equal the binding energy of the atomic phase per two atoms.

Consider a reacting mixture of N atoms and N_2 molecules. Let x be the fraction of molecules that have undergone dissociation into atoms. We write F the free energy per two atoms as;

$$F = (1 - x)\, F^0_{N_2} + xF^0_{2N} + F_{mix} + A_{int} + xE_b \quad , \tag{9}$$

where $F^0_{N_2}$ and F^0_{2N} are respectively the free energies of the isolated molecule and of two atoms. F_{mix} is the free energy of mixing;

$$F_{mix} = kT(1 - x)\ln((1 - x)/(1 + x)) + kT2x\ln((2x/(1 + x)). \tag{10}$$

A_{int} is the nonideal free energy or the excess free energy arising from the interaction of the two components. A_{int} can be written in terms of fluid variational theory as:

$$A_{int} = A^o_{ref} + (1 - x)^2 \frac{N^2}{2V} \int \phi_{N_2-N_2}(r)\, g(r, d_{N_2-N_2})\, d^3r$$

$$+ 2(1 - x)\, x \frac{N^2}{2V} \int 2\, \phi_{N-N_2}(r)\, g(r, d_{N-N_2})\, d^3r$$

$$+ x^2 \frac{N^2}{2V} \int 4\, \phi_{N-N}\, g(r, d_{N-N})\, d^3r \tag{11}$$

A^0_{ref} is the reference free energy of the mixture which at this point will remain unspecified. The additional factors 2 and 4 enter into the expression because the free energy has been defined in units of 2 atoms in the form of molecules or atoms. Thus each integral represents respectively the interaction of two molecules, two times the interaction of one molecule with one atom, and four times the interaction of a pair of atoms.

We have already shown that the intermolecular potential (eq. 1) accurately reproduces the experimental Hugoniot up to 310 kbar. At this point we introduce an approximation for the intermolecular forces of the N-N and $N-N_2$ interaction. The shock data suggests that at the conditions considered in this study liquid nitrogen is a complex mixture of interacting molecules,

atoms and ions with a rich variety of excited electronic, vibrational and chemical states. A proper calculation demands that the properties of all these states be obtained and their ensemble averages determined by minimizing the free energy with respect to composition. This represents a formidable undertaking. Instead we have made several approximations which we consider plausible in light of all the uncertainties and which also have the advantage that they considerably simplify the statistical mechanical theory.

We constructed model atom-atom and atom-molecule potentials from a knowledge of the N_2-N_2 potential. The energy of interaction of a single N atom with an N_2 molecule is to be approximated as one-half the interaction energy of two molecules.

$$\Phi_{N_2-N} = \frac{1}{2} \Phi_{N_2-N_2} .$$

Similarly the energy of interaction between two atoms is one half that of an atom and a molecule or one-fourth that of the molecule-molecule energy.

$$\Phi_{N-N} = \frac{1}{2} \Phi_{N-N_2} = \frac{1}{4} \Phi_{N_2-N_2}$$

By making these approximations and assuming the existence of a single averaged hard sphere diameter the expression for A_{int} of the mixture reduces to:

$$A_{int} = A^0_{ref} + \frac{1}{2} \frac{N^2}{V} \int \Phi_{N_2-N_2}(r)\, g(r, d)\, d^3r \qquad (12)$$

which is the same expression as for the pure fluid.

As a consequence of these approximations the nonideal energy of the fluid, the part resulting from the interatomic interactions, remains unchanged by the dissociation. The only changes in the total free energy come from the compositional changes in the internal degrees of freedom of the two species

and the mixing entropy. Our method for constructing the intermolecular potentials was inspired by some earlier work of Amdur et al.[12] and Vanderslice et al.[13] They approached the problem in the reverse direction. They first determined an atom-atom potential from approximate Valence Bond theory. They then obtained an N-N_2 potential and then an N_2-N_2 potential by averaging over all angles of the N-N interaction. Instead we have reversed the procedure by starting out with an N_2-N_2 pair-potential (Eq. (1)) which fits the molecular phase shock data. However the essential idea is the same. It assumes that interatomic forces can be built up from atom-atom interactions.

The alternative procedure which is to carry out rigorous quantum mechanical calculations of the N-N and N-N_2 potentials is unlikely to be useful in the present case since we are dealing with a fluid that is three times normal liquid density and many body chemical interactions of the nitrogen atom will be important. For example the N-N potential is known from the vibrational properties of the N_2 molecule. But to use this potential in a dense atomic fluid is to assume that every nitrogen atom forms a diatomic molecule with each of its neighbors. This leads to a binding that is too strong and leads to unrealistically large amounts of dissociation at relatively low temperatures.[14]

The present approximation carries with it the advantage that it greatly simplifies the statistical thermodynamics and as will be shown below permits us to use the law of mass action rather than the more complicated free energy minimization for a multi-component system.

Minimization of F (Eq. (9)) with respect to x gives:

$$x^2 = \frac{\beta}{4 + \beta} \tag{13}$$

where

$$\beta = \exp\left[-\left(F^0_{2N} + E_b - F^0_{N_2}\right)/KT\right]$$

and

$$\beta = \frac{\left(q_t^N q_e^N\right)^2}{q_t^{N_2} q_r^{N_2} q_v^{N_2} q_e^{N_2}} e^{-(D_e + E_b)/KT} \tag{14}$$

D_e is the depth of the oscillator well and for N_2 and has the value 9.91 ev. D_e is related to the dissociation energy D_o by $D_e = D_o + 1/2$ $h\nu$. The q's are the atomic and molecular partition functions defined earlier. The pressure and energy are calculated as in the case of the pure fluid. The expressions for the energy and pressure of the mixture are:

$$E = 3/2\ (1 + x)\ RT + U_{int} + (1 - x)\ E^{N_2}_{rve} + (1 - x)\ D_e + 2x\ E^N_e + xE_b. \tag{15}$$

and

$$P = (1 + x)\ RT/_V + P_{int} + xP_b \quad , \tag{16}$$

where $P_b = -\ \partial E_b/\partial V$.

E^N_e is the electronic energy of a single atom. For atomic nitrogen the electronic partition function can be written:

$$q^N_e = 4 + 10\ \exp(-\ 2.38/T) + 6\exp(-\ 3.58/T) \tag{17}$$

It will be shown that at the conditions of interest atomic nitrogen is a degenerate metal. We assume it is an expanded metallic fluid with an electronic structure made up of a filled 2s band and three degenerate 2p-like conduction bands. The justification for this step will become apparent further on. This picture is one in which the electronic energy levels approach their atomic limit at low density. This leads to a value of

$$q_e^N = 3 \tag{18}$$

for ground state of the electronic partition function replacing Eq. (17).

A rigorous calculation of the atomic phase binding energy E_b is beyond the scope of the present paper. Instead we have chosen this term to be a volume dependent function which is obtained from a fit to the principal Hugoniot and is required also to be in agreement with the 0 K isotherm of the metal obtained by McMahan[1,15] using electron band theory and discussed later in the next section.

We write the volume dependent dissociation energy as:

$$D = D_e + E_b \qquad V < 20 \text{ cm}^3/\text{mol}.$$

$$D = D_e \qquad V > 20 \text{ cm}^3/\text{mol}$$

$$\text{where } E_b = -A(20 - V)^2 \text{ and } D_e = 9.91 \text{ ev}. \tag{19}$$

With this model good agreement is obtained with measured shock pressures and temperatures by using a value for A of 0.045 (curve C) or 0.050 (curve D) as shown in Figs. 1 and 2. Table 1 lists some of the properties calculated along curve C. Values of D and x along curve D are plotted in Fig. 3. An interesting feature regarding these curves is that they approach $V_o/V = 4$

($V = 8.6\ cm^3/mole$) as a limiting compression which is the value one expects for a monatomic or fully dissociated diatomic gas.

An important thermodynamic consequence of the decreasing dissociation energy is that P_b will have negative values for $V < 20\ cm^3/mole$. In physical terms Eqs. (15) and (16) state that for each molecule that dissociates, the two atoms are converted into metal atoms lying on a much lower isotherm (see Fig. 5). Thus the dissociation process leads to a drop in total pressure of $P_b x$ at constant volume or equivalently to a volume collapse at fixed pressure.

Up to nearly 310 kbar and 7300 K the fraction of dissociated molecules is small (1%) but above this pressure the dissociation rises rapidly absorbing shock energy and leading to the S-like behavior of the shock temperature curve. The negative contribution to the pressure ($P_b x$) arising from the cohesive bonding of the metal phase leads to the large increase in the compressibility observed along the Hugoniot. This is illustrated in Fig. 4 which plots the ratio of $P_b x$ to the total Hugoniot pressure. An analogous behavior has been observed in shock compressed liquid argon and xenon. In these liquids electrons are thermally excited from the top of a filled p-like valence band to the bottom of an unfilled d-like conduction band in which they have a lower pressure. This means the energy band gap separating these two states is decreasing with decreasing volume. This introduces a negative contribution to the pressure just as it does in the present case. And with the same effect. In the case of N_2 it is the dissociation energy rather than the electron band gap that is decreasing with compression and makes the negative contribution.

C) Metallic Nitrogen

An examination of the data in Table 1 shows that at these densities atomic nitrogen forms a degenerate metal. For example at a Hugoniot pressure of 640 kbar or 10 cm^3/mol-N_2. the calculated fraction of dissociated molecules is 0.37. Since each molecule forms two atoms the atom concentration is 0.74 N/V atoms/cm^3. Based on the band structure we assumed earlier there are 2 electrons in the 2s state and one in each of three degenerate 2p-like conduction bands. A free electron approximation of the band width leads to a Fermi energy of 4.6 eV. This is considerably higher than the 13000 K (1.1 ev) shock temperature. Thus under these conditions atomic nitrogen may be considered as a degenerate metal with a negligible temperature dependence and an electronic ground state of three. It may be argued that the conduction band should contain 5 electrons in which case the Fermi energy would be 13.5 eV. at these conditions and metallic nitrogen would be an even more degenerate. As a point of reference the reader should note that 10 cm^3/mole-N_2 is 5 cm^3/mole-N which is two times the density of normal aluminum.

The Hugoniot calculations are rather sensitive to the precise value of Q_e^N. Calculations were also made using the atomic electronic partition function (Eq. (20)). These lead to Hugoniot curves which are similar to those in Fig. 1 and agree with experiment. However since this function has a much larger heat capacity it leads to shock temperatures that are too low (Fig. 5).

In the limit of x = 1 and T = 0 K Eqs.(21) and (22) reduce to expressions for the energy and pressure of the pure metallic phase:

$$E_{2N} = U_{int} + E_b \tag{19}$$

and

$$P_{2N} = P_{int} - \partial E_b/\partial V \tag{20}$$

where $U_{int} = 1/2 \sum_{ij}^{'} \phi_{N-N}$ is the lattice energy obtained by summing over all lattice sites and $P_{int} = - \partial U_{int}/\partial V$. These equations are similar to many empirical equation of state models which have been constructed using a sum over atom-atom interactions and a term to represent the volume dependent binding energy and electron kinetic energy. A well known example is the Pseudopotential Theory for simple metals.

Figure 6 provides an overview of the nitrogen equation of state for the present model showing the 0 K molecular and metallic isotherms and the Hugoniot. U_{int} and P_{int} were calculated for a bcc lattice. McMahan has calculated isotherms for atomic nitrogen in several different crystal structures using the linear muffin tin orbital (LMTO) method.[1,14] His results are also shown in Fig. 6. The hcp isotherm, not shown, lies very close to and slightly below the fcc curve. Table 2 compares the calculated energies at the largest volume studied by McMahan (9.09 $cm^3/mol.N_2$). The overall agreement of the present model with McMahan's results, between bcc and the more open sc, are consistent with what one would expect from having determined empirically the binding energy from expanded liquid metal data. At higher pressure our isotherms approach those of McMahan's close packed structures. Thus we see the pressure drop on dissociation P_b is given by the change in pressure on going from the molecular to the metallic state, and E_b is the change in binding energy.

Kerley and Switendeck[9] have recently reported theoretical calculations for nitrogen. They used a fluid model which like ours is based on hard sphere

theory. But they use band theoretical models to obtain a metal phase equation of state. In principal their method should provide an accurate determination of the binding energy. In practice they found it necessary to introduce an additional binding energy of roughly half the molecular dissociation.

In retrospect it appears that the binding energy and its volume dependence could have been obtained directly from McMahan's results alone by fitting E_b to Eqs. (19) and (20). Although it may not be apparent a-priori which is the correct crystal structure. These results do suggest a procedure by which dissociation curves for other dense molecular liquids such as hydrogen could be calculated using the metallic properties.

Doubly Shocked Nitrogen

A) Reflected Hugoniots

Up to now our discussion has been restricted to examining the single shock or principal Hugoniot. Measurements have also been made for doubly shocked nitrogen up to 1.1 Mbar. In these experiments the first shock after traversing the sample is reflected off of a stiff end plate material such as copper. By measuring the shock velocity in this metal and impedance matching with nitrogen one can determine the pressure and density of the twice shocked liquid. Figure 7 compares the data of Nellis et al.[4] with the theoretical calculations. The pressures reached along the Hugoniot by the first shocks are labeled as A-E and the respective reflected experimental points (A'-E') are identified by the error bars. The solid and dashed curves are theoretical calculations. All the calculated reflected curves are found to fall within the narrow shaded band. These calculations correctly predict the unusual feature of a reflected Hugoniot lying above the principal Hugoniot. They are

also in excellent agreement with the experimental points (D'-E') at 0.84 and 1.11 Mbar. However we have been unable to obtain agreement with the points (A'-C') despite some considerable amount of 'experimentation' using a number of hypothetical models. Consequently we have been forced to entertain the possibility that these are not equilibrium states. To test this we made calculations which assume that for points A'-C' the relaxation time for dissociation is longer than the experimental resolution time (10^{-9} sec.). In other words these states do not undergo dissociation. The predicted reflected shock points, shown by the dashed curves, although shifted to higher pressures are still too low. The improved agreement suggests that nonequilibrium effects may be a factor.

Very little is known about relaxation rates at liquid shock conditions. Vibrational relaxation rates extrapolated from shock tube results[16] by scaling the density predict equilibrium times of 10^{-10} sec., an order of magnitude less than the experimental resolution time. Such an extrapolation assumes that only binary collisions are important so that actual times are likely to be even shorter. Rotational relaxation is more rapid than vibrational and can be assumed to be in continuous equilibrium with the translational temperature. Molecular dissociation rates for gases have been measured in shock tubes.[17] We scaled these rates to liquid densities using hard sphere collision rate theory.[18] The scaled dissociation times for the conditions of the shock experiments were in the range 0.02-1.1 ns. These times are much less than the time resolution of the temperature and conductivity measurements and less than the time resolution of the equation-of-state experiments. Consequently we expect non-equilibrium effects to be small in all the experiments.

B) Reflected Temperatures and Shock Cooling.

Possibly the most fascinating and illuminating feature of the nitrogen measurements are the reflected shock temperatures which in one experiment actually shows evidence of a cooling. In Fig. 8 the experimental points are compared with theoretical calculations. We find that the shock cooling is extremely sensitive to the binding energy. For example double shock temperatures calculated using A = .045 in the binding energy show very little decrease. Whereas calculations using A = 0.050 and shown in the figure predict shock cooling and are in fair agreement with experiment. In general the size of the experimental error makes it difficult to evaluate the goodness of the theory. In Fig. 9 the dissociation energy in the reshocked states has been held constant at their initial values along the principal Hugoniot. This leads to a much smaller degree of dissociation and to reflected temperatures all of which increase with temperatures. This is shown in Fig. 10 where we have plotted the degree of dissociation versus volume for each model along the upper most theoretical curves of Figs. 8 and 9. The calculated temperatures are indicated at several points. As the dissociation becomes large and approaches its limit near x = 0.7 the temperature begins to increase again.

The reflected shock temperatures are clearly related to the degree of dissociation. We have already seen in Figs. 1 and 2 that along the principal Hugoniot the dissociation which is an endothermic process causes a lowering in the pressure and temperature rise with compression. In the case of reflected shocks their paths approach the isentrope and they undergo relatively small temperature rises. In this regard it is important to recognize that in the shock process a fixed amount of kinetic energy is delivered impulsively to a sample. This energy will be partitioned amongst the various degrees of freedom to achieve an equilibrium final state. If the dissociation energy

were decreasing with compression this would lead to an increase in the dissociated fraction even if there were no temperature rise. Thus if the degree of dissociation is sufficiently large during reshock then coupled with a near isentropic process some energy must be removed from the translational and vibrational modes which leads to a cooling. If there were no change in the dissociation energy along the reshock path, as is the case in the lower curve shown in Fig. 10, then a temperature rise will take place accompanied by only a small increase in the dissociation. Clearly the degree of volume dependency in the dissociation energy controls the amount of temperature rise and fall.

Discussion

The model described in this paper is an approximation to a very complicated situation. Our primary intent has been to acquire an understanding of the underlying physics. The key to the success of the present model is the cohesive energy of the atomic phase which introduces an effective volume dependent dissociation energy. This determines the metal equation of state and it is the binding energy of the metal which causes the considerable softening of the Hugoniot. Although we have assumed a metallic-like atomic phase in fact this phase might very well include a mixture of doubly bonded molecules and short chains of N polymers. Our model does not provide a unique description of the chemical composition. Additional models can no doubt be constructed to agree with the data. But we do believe that the important feature of a volume dependent dissociation energy will need be an essential feature. The method by which we approximated the metallic N-N potential is open to argument. But since any realistic calculation of this

property at these conditions must involve a considerable effort and is unlikely to provide quantitative results in any case we chose, as a first try, the intuitive procedure which also greatly simplified the ensuing thermodynamics. In general the model succeeds in calculating the pressures and temperatures along the principal Hugoniot in agreement with experiment.

The observation of shock cooling provides strong evidence that the effective dissociation energy must be decreasing with compression. We believe that this is a general phenomena of reflected shocks and should be observed in liquid argon, xenon and CsI, materials which have electron band gaps that decrease with compression. Work is now proceeding along these lines.

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Table 1. Theoretical Hugoniot

Initial conditions are V_o = 34.7 cm^3/mole, T_o = 77.6 K, P_o = 0.0 kbar.

V cm^3/mol	P(kbar)	T(K)	D(eV)	x
34.7	0.0	77.6	9.91	0
22.00	21.0	418	9.91	0
20.00	40.8	821	9.91	0
18.00	79.2	1656	9.71	10^{-14}
16.00	156.8	3502	9.11	10^{-6}
15.00	224.2	5234	8.66	5×10^{-4}
14.00	308.9	7333	8.11	0.011
13.00	389.9	8936	7.46	0.047
12.00	466.4	10033	6.71	0.113
11.00	542.4	10808	5.86	0.218
10.00	623.1	11477	4.91	0.377
9.50	671.3	11978	4.40	0.487
9.00	742.1	13196	3.86	0.631
8.71	845.0 kbar	16000	3.54	0.750

Table 2. Energy of Metallic Nitrogen

T = 0 K, V = 9.09 cm^3/mole-N_2

	E(Ry/atom)
Model C (A = .045)	- 0.1259
Model D (A = .050)	- 0.1455
bcc, reference 14	- 0.1277
sc, reference 14	- 0.2021

FIGURE CAPTIONS

Fig. 1 Liquid nitrogen Hugoniots, $V_0 = 34.7$ cm^3/mole. Experimental data from Ref. 4(|-•-|) and Ref. 11 (|-o-|). Theoretical curves are discussed in the text. A does not include dissociation. B includes dissociation to atoms using a constant value of the dissociation energy (9.76 eV). C and D include a binding energy of the monatomic phase with values respectively of A = 0.045 and 0.050 in Eq. (20).

Fig. 2 Liquid nitrogen shock temperatures, $V_o = 34.7$ cm^3/mole. Experimental data from reference 5. Theoretical curves follow the same caption as in Fig. 1.

Fig. 3 Dissociation energies (D) and fractions of dissociated molecules (x) calculated along theoretical Hugoniot curve D in Figs. 1 and 2.

Fig. 4 The ratio of cohesive pressure $P_b x$ to total Hugoniot pressure P_H versus volume.

Fig. 5 Comparison of shock temperatures calculated with metal ($Q_e^N = 3$), and atomic (Eq. (17)) partition functions designated respectively by solid and dashed curves.

Fig. 6 Molecular and atomic nitrogen equation of state. The dashed curves represent the results of McMahan. The theoretical curve is described in the text and was calculated using the binding energy obtained by fitting the present model to the Hugoniot. P_b is the pressure drop on dissociation.

Fig. 7 Reflected shock pressures. The letters A-E designate the first shock starting points along the principal Hugoniot and A'-E' are the final reflected points. The bars represent experimental data from Ref. 5. The shaded area represents the locus of 'equilibrium' theoretical calculations. Dashed lines are calculations which omit dissociation and are nonequilibrium calculations.

Fig. 8 Reflected shock temperatures for liquid N_2. The initial experimental points along the principal Hugoniot and final points (bars) are designated by the same symbols. The solid curves were calculated as described in the text using the volume dependent dissociation energy. The calculated dissociated fraction is shown in parenthesis.

Fig. 9 Reflected shock temperatures for liquid N_2. Experimental data follows the same caption as in Fig. 8. The dashed curves were calculated using a dissociation energy held constant at its value along on the principal Hugoniot. The calculated dissociation fraction is shown in parenthesis.

Fig. 10 The degree of dissociation (x) along Hugoniots relected from V = 12.5 cm^3/mol. plotted versus volume for each model indicated in the text. The calculated temperatures are shown for several points.

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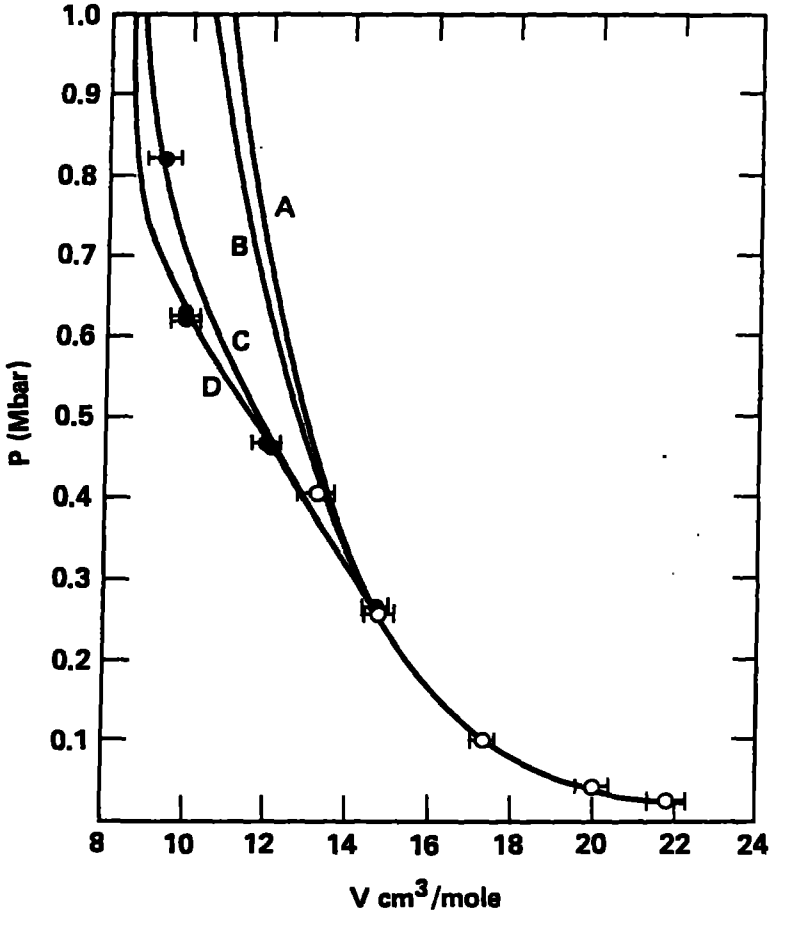
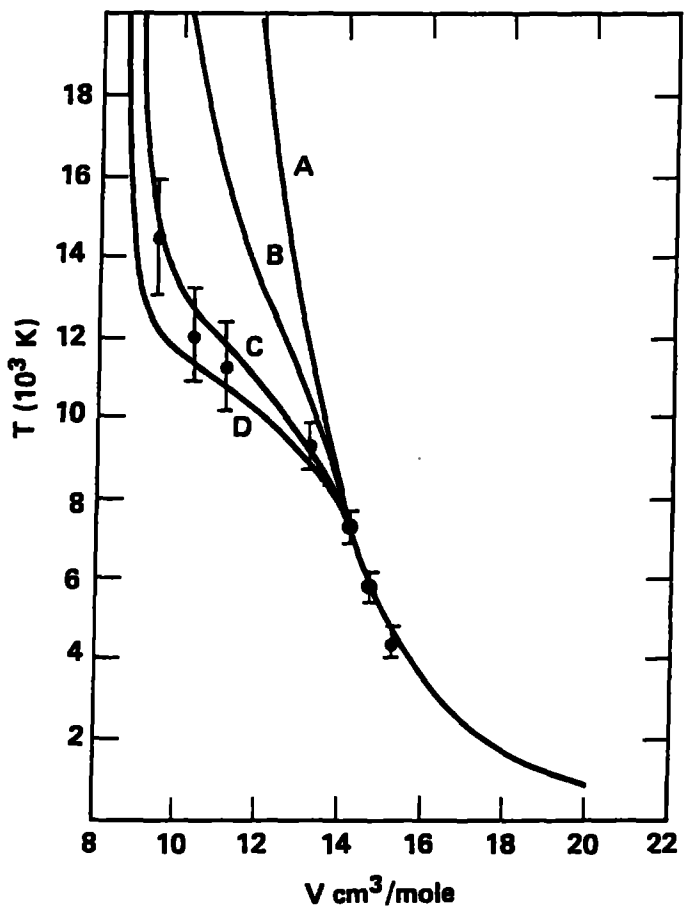

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
P (Mbar)
A
B
C
D
8
10
12
14
16
18
20
22
24
V cm3/mole

Figure 1



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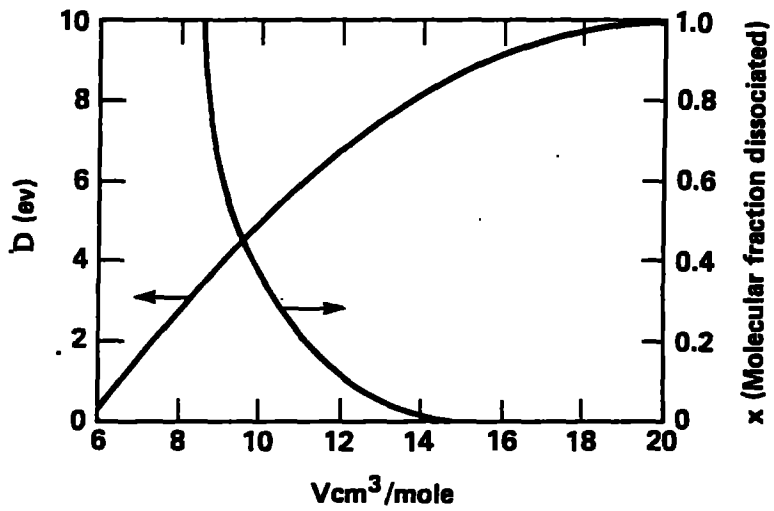

10
8
6
4
2
0
D (ev)
1.0
0.8
0.6
0.4
0.2
0
x (Molecular fraction dissociated)
6
8
10
12
14
16
18
20
Vcm3/mole

Figure 3

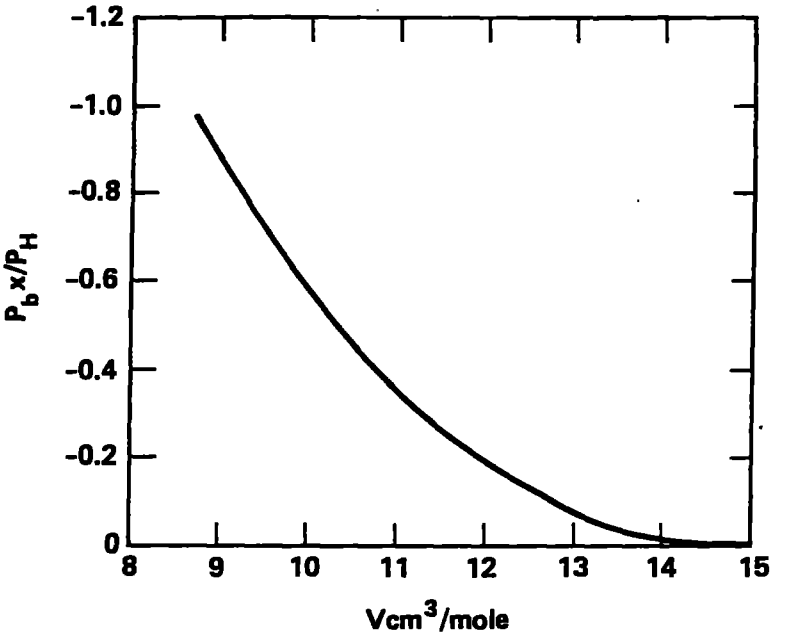
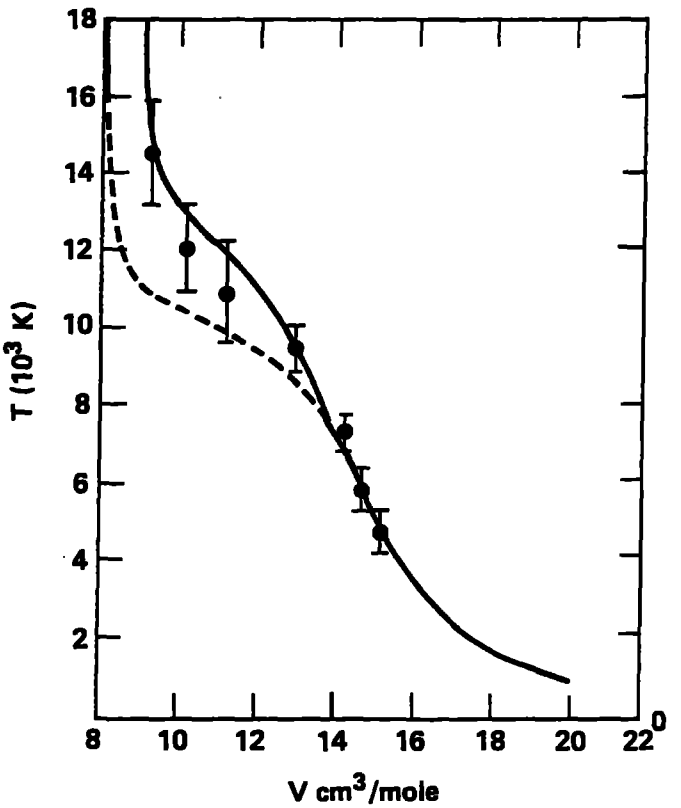


Figure 4



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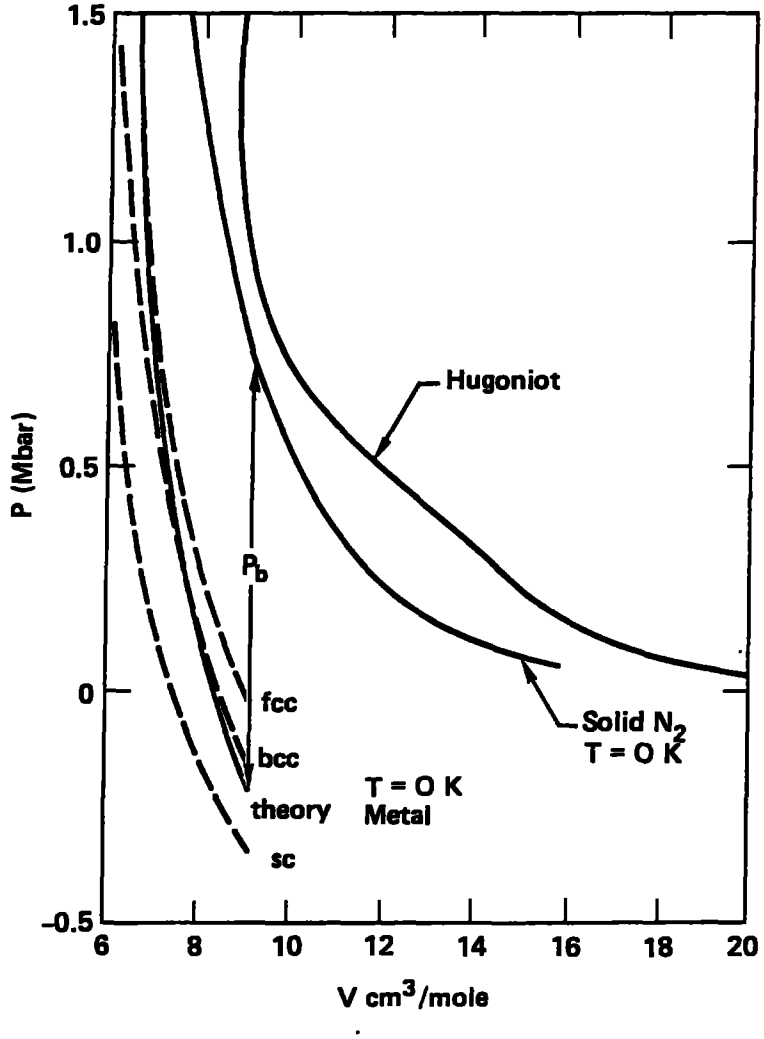
1.5
1.0
0.5
0
-0.5
P (Mbar)
6
8
10
12
14
16
18
20
V cm^3/mole
Hugoniot
P_b
fcc
bcc
theory
sc
T = O K
Metal
Solid N_2
T = O K

Figure 6

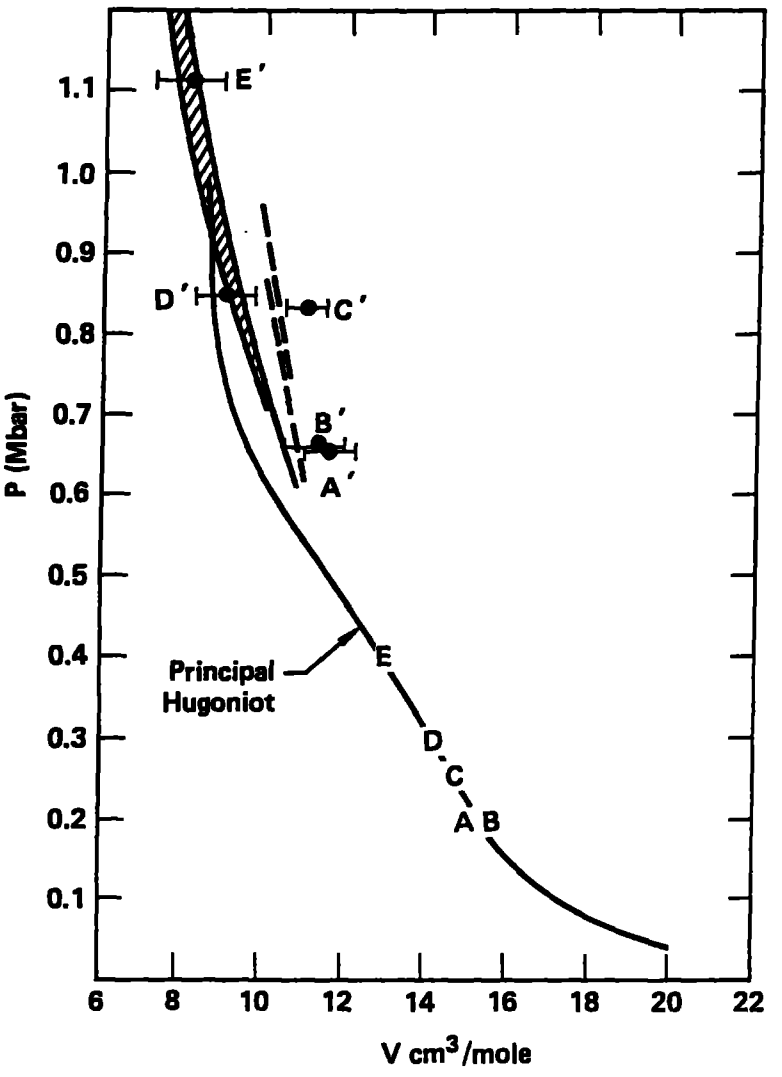
E'
D'
C'
B'
A'
Principal
Hugoniot
E
D
C
A
B
P (Mbar)
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
6
8
10
12
14
16
18
20
22
V cm3/mole

Figure 7

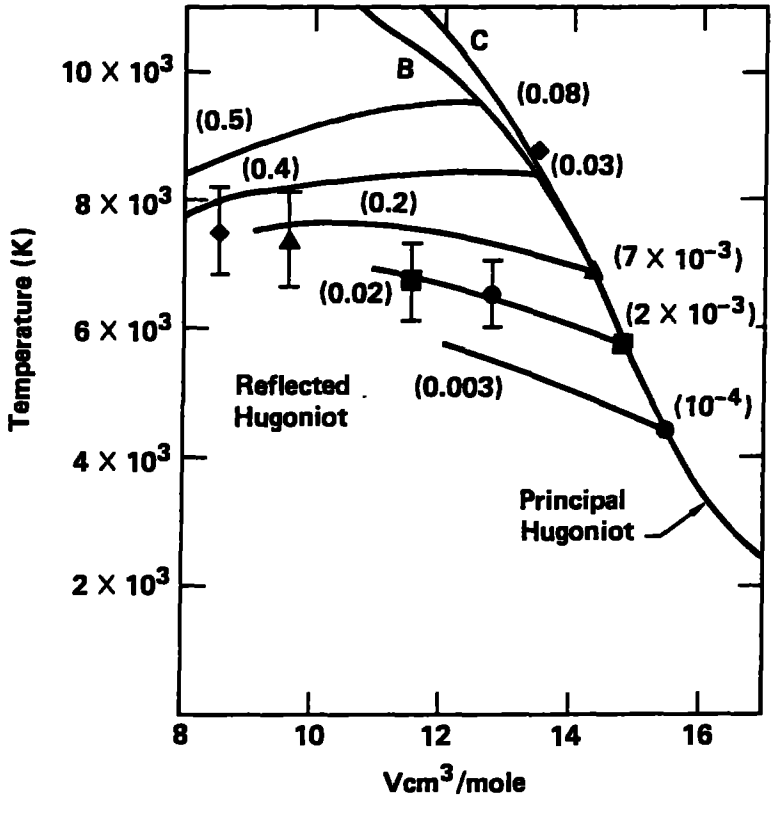
C
B
(0.08)
(0.5)
(0.03)
(0.4)
(0.2)
(7 X 10⁻³)
(0.02)
(2 X 10⁻³)
Reflected Hugoniot
(0.003)
(10⁻⁴)
Principal Hugoniot
10 X 10³
8 X 10³
6 X 10³
4 X 10³
2 X 10³
Temperature (K)
8
10
12
14
16
Vcm³/mole

Figure 8

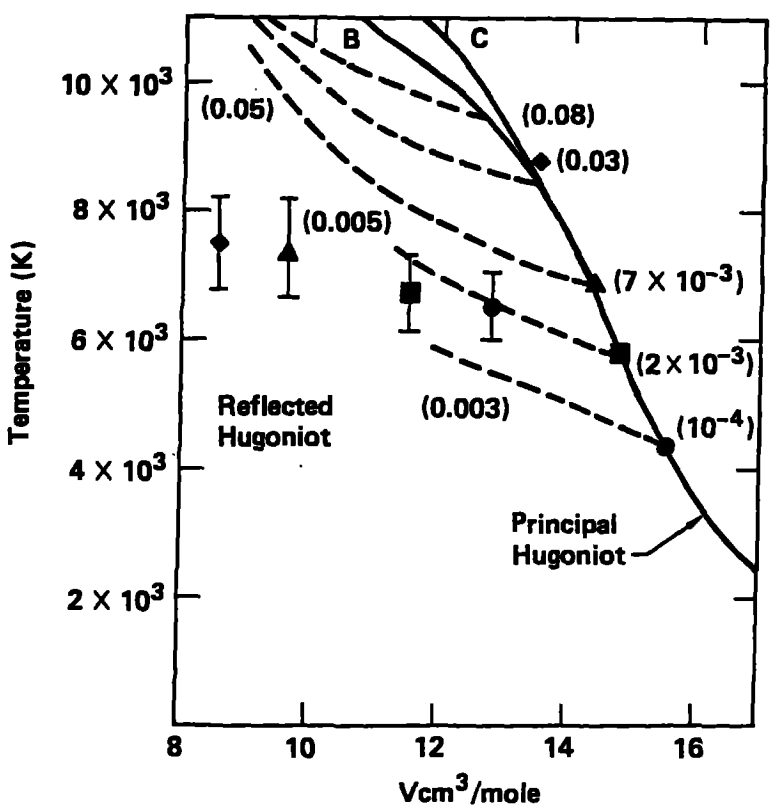
B
C
10 X 10^3
8 X 10^3
6 X 10^3
4 X 10^3
2 X 10^3
(0.05)
(0.08)
(0.03)
(0.005)
(7 X 10^-3)
(2 X 10^-3)
(0.003)
(10^-4)
Reflected Hugoniot
Principal Hugoniot
Temperature (K)
8
10
12
14
16
Vcm^3/mole

Figure 9

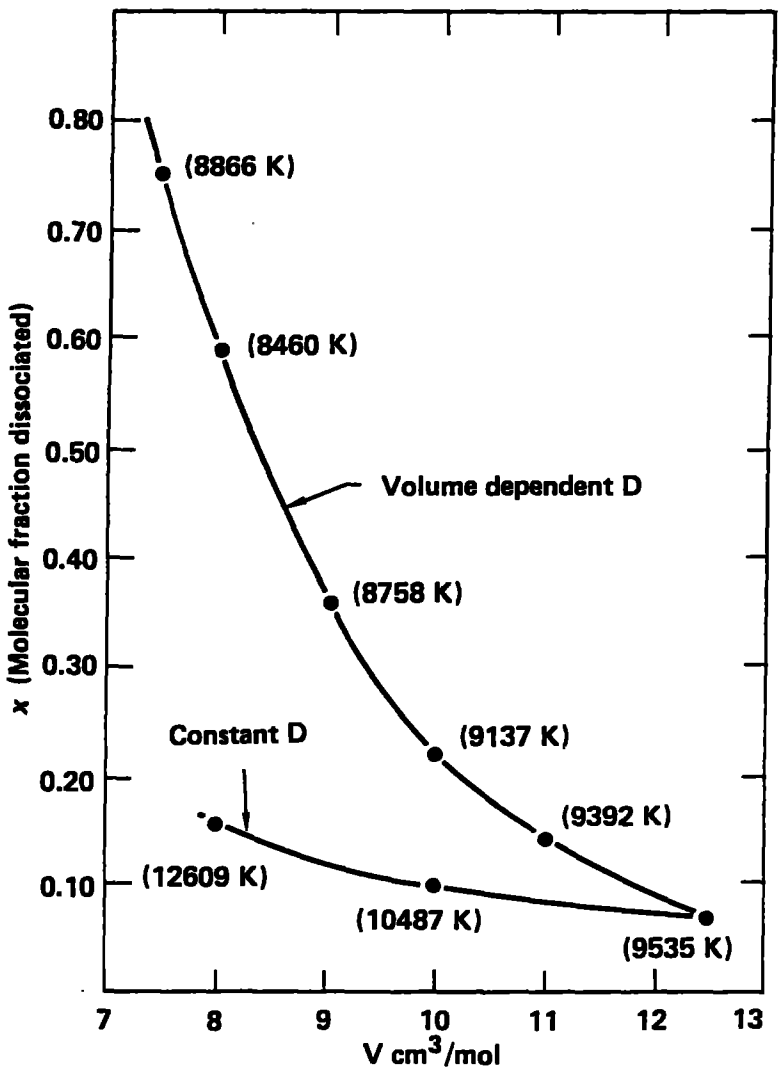
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
x (Molecular fraction dissociated)
(8866 K)
(8460 K)
Volume dependent D
(8758 K)
(9137 K)
Constant D
(9392 K)
(12609 K)
(10487 K)
(9535 K)
7
8
9
10
11
12
13
V cm3/mol

Figure 10